

PATENT SPECIFICATION

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(54) DESULPHURISATION PROCESS

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2., England, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 This invention relates to a process for the desulphurisation of olefinic streams.

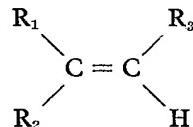
15 Olefin streams derived from petroleum feedstocks are frequently contaminated with small quantities of sulphur and/or sulphur-containing compounds. The presence of such materials is often undesirable since, inter alia, they are powerful poisons for many olefin conversion catalysts.

20 It is an object of the present invention to provide a process for reducing or substantially eliminating sulphur-containing materials from olefin streams.

25 Thus according to the present invention there is provided a process for the desulphurisation of an olefinic feedstock which process comprises contacting the feedstock with supported elemental nickel under conditions such that residual sulphur is adsorbed by the nickel. It is an advantage of the process that hydrogen sulphide is not liberated during the desulphurisation.

30 The preferred feedstocks contain C_2-C_{20} olefins, especially C_4 olefins.

35 In particular, the process is very suitable for treating feedstocks containing highly reactive olefins of general formula



40 wherein R_1 and R_2 are alkyl groups and R_3 may be an alkyl group or hydrogen. Feedstocks containing such olefins can be desulphurised with little or no formation of heavy polymeric material.

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The feedstock is passed over supported elemental nickel, which takes up residual sulphur and becomes progressively sulphided. It has been found that the presence of a small amount of hydrogen is beneficial, even though the process is not a hydrodesulphurisation process because no hydrogen sulphide is produced. The beneficial effect of hydrogen is believed to be due to the fact that the sulphur is present in organic sulphur compounds and that, as the sulphur is adsorbed on nickel, unsaturated organic radicals are produced which tend to polymerise on the nickel surface and reduce its catalytic activity. If hydrogen is available these radicals are hydrogenated to harmless more saturated hydrocarbons. The maximum amount of hydrogen needed to achieve this can be calculated and is very small.

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If desulphurisation is carried out in the liquid phase, then the quantity of hydrogen necessary can be simply that amount which dissolves in the feedstock.

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If desulphurisation is carried out in the vapour phase, then the equilibrium hydrogen partial pressure should be greater than the minimum necessary to prevent catalyst deactivation but less than that at which an intolerably high level of hydrogenation of the olefinic hydrocarbon occurs.

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If hydrogen is present in excess, there is a risk of hydrogenating the olefinic feedstock to some extent. The hydrogenating effect of nickel declines as the amount of sulphur combined with it increases. Thus by pre-sulphiding the catalyst to a sulphur/nickel ratio such that the nickel has no hydrogenation activity at the temperatures and pressures used for desulphurisation, thus risk can be avoided. However, an excess of hydrogen is not preferred under normal conditions.

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A suitable process for pre-sulphiding the catalyst is described in our British Patent Specification No. 1144498 and FP 1,498,697.

[Price 25p]

- The supported nickel catalyst used may incorporate any of the known natural or synthetic support materials, such as the refractory oxides of elements of Groups II to V of the Periodic Table or kieselguhr, pumice or sepiolite. Sepiolite is the preferred material and the preferred catalyst is nickel on sepiolite prepared according to the disclosures of British Patent No. 899652. Sepiolite is the preferred support because it can withstand high temperatures under reducing or oxidising conditions, it holds the nickel in finely divided form and with a high surface area, and it is relatively cheap.
- 15 Supported nickel catalysts, e.g. nickel on sepiolite prepared according to the above men-

tioned British patent, may contain from 1—50% weight nickel (expressed as elemental nickel) and more particularly from 5—25% weight. Such a catalyst has high nickel surface area and has high activity and selectivity for the desulphurisation of olefins. It is capable of adsorbing sulphur up to a sulphur:nickel atomic ratio of at least 0.75:1. Since the sulphur capacity of the supported nickel material is high and is known, it is possible to provide a sufficient amount of it to give an economic catalyst life.

The reaction conditions for the desulphurisation may be selected from the following ranges:

	Temperature	0 to 350°C (preferably RT to 250°C)
	Pressure	0 to 2000 psig (preferably 50 to 1000 psig)
	Space velocity over the supported nickel	0.01 to 20 LHSV (preferably 0.1 to 2.0)
35	Inlet hydrogen: hydrocarbon ratio on total feed	nil to 1:1 molar (preferably 0.001 to 0.1:1 molar)

(By "RT" we mean room temperature i.e. ca 20°C to 25°C)

For a supported nickel catalyst there is a "threshold" temperature. Above this temperature the catalyst acts as a conventional hydrogenation catalyst in the presence of hydrogen but below it hydrogenation occurs only to a limited extent. Below the threshold temperature, however, the supported nickel material is capable of adsorbing sulphur. The threshold temperature is comparatively low when the supported nickel material is fresh, but as it adsorbs sulphur, and thereby becomes sulphided, the threshold temperature increases. The sulphur capacity of the supported nickel increases with increasing temperature, so that by progressively increasing the operating temperature so that this is just below the threshold temperature the full capacity of the supported nickel may be used. The adsorption effect is believed to be a massive effect, i.e. it is not merely a surface phenomenon, and the limit of sulphur capacity occurs when the nickel is sulphided in depth. At temperatures below 200°C the sulphur capacity of the nickel-on-sepiolite material depends on the type of sulphur compound present in the feedstock but at temperatures above 250°C the ultimate sulphur capacity gives a sulphur:nickel atomic ratio of at least 0.75:1.

65 Relatively mild reaction conditions are

employed in a process according to the present invention, and, in contrast to hydrosulphurisation, no separation of sulphur-containing materials from the product stream is necessary.

The invention is illustrated by the following examples.

EXAMPLE 1

- a. *Desulphurisation Catalyst*
10% nickel-on-sepiolite (3—60 BSS) treated for 24 h in H₂ (GHSV 100) at atmospheric pressure and 300—320°C.
- b. *Desulphurisation Conditions*
Pressure 300 psig
Feed Rate 0.5 LHSV
Feed saturated with H₂ at 80 psig (ca 0.4% molar)
- c. *Feed Composition* % wt.

Propane	1.0
Isobutane	1.4
n-butane	9.1
Butene-1	2.3
Isobutene	43.5
Butene-2	42.7
Sulphur	2.3 ppm
- d. *Results*

Time on Stream	h	24	48	72	96
Temperature	°C	25	25	25	75
Sulphur content of product	ppm	0.8	0.8	1.6	0.6
*Material >C ₄ collected (% wt of feed)		1.9	0.6	Not Detected	Not Detected

*mostly i-C₄ oligomers

EXAMPLE 2

- a. Desulphurisation Catalyst
As Example 1.

- 5 b. Desulphurisation Conditions
As Example 1 but,
Temperature 25°C
Feed saturated with H₂ (ca 0.4% molar) for first 60 HOS and after
10 160 HOS

c. Feed Composition

	% wt.
Isobutane	3.0
n-butane	8.3
Butene-1	4.3
Isobutene	45.8
Butene-2	38.6
Sulphur	2.1 ppm

d. Results

Time on Stream	h	8	26	50	74	156	180
Hydrogen: Total Hydrocarbon Ratio (% molar)		0.4 (Appr.)	0.4 (Appr.)	0.4 (Appr.)	Nil	Nil	0.4 (Appr.)
Sulphur Content of product (ppm)		0.7	0.3	0.4	1.0	1.0	0.5

- Example 1 shows that, despite the presence of 43.5% isobutene, heavy material was formed in substantial amounts only during the initial part of the run. The effect of temperature increases on the sulphur capacity of the catalyst is also illustrated since after three days the desulphurisation efficiency of the catalyst had been reduced as the sulphur content of the catalyst approached saturation at 25°C but further removal of sulphur, without increased formation of heavy material occurred when the temperature was raised to 75°C.
- 25 Example 2 illustrates the advantage of using small quantities of hydrogen in the process.
- 30 35 a. Catalyst

- 10 per cent Nickel-on-Sepiolite (30—60 BSS) activated in H₂ (100 GHSV) at atmospheric pressure for 24 h at 300—
40 320°C

b. Feedstock

Butadiene Raffinate containing :—	
isobutane	2.3 per cent
n-butane	8.7
isobutene	42.4
n-butene	46.6
sulphur	16 ppm (added as tetrahydrothiophene)

The feedstock was saturated with H₂ at 80 psig and 20°C (ca 0.4 per cent molar)

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c. Reaction Conditions

Feed Rate	LHSV : 1.0
Pressure	psig : 150
Temperature	: 25

rising to 250°C (see below)

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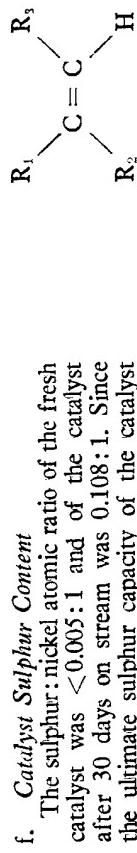
d. Desulphurisation

Days on Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sulphur Content of Reactor Effluent	ppm	0.5	0.4	—	1.6	6.8	4.0	1.6	—	—	2.3	3.2	0.7	1.3	1.2	—
Reaction Temperature	°C	25	25	25	25	75	100	150	150	150	150	180	180	180	180	180

Days on Stream	17	18	19	20	21	22	23	24	25	26	27	28	29	—	
Sulphur Content of Reactor Effluent	ppm	—	1.4	2.2	2.2	1.4	3.3	—	—	4.2	5.7	4.0	2.1	1.7	—
Reaction Temperature	°C	180	180	180	180	180	180	200	200	230	230	230	230	230	230

e. *Polymerisation*
During the run no polymerisation of olefins was detected except; on days 1 (0.9 per cent of feedstock), 12 (0.8 per cent), 28 (0.8 per cent) and 29 (0.7 per cent).

3. The process according to claim 2 wherein the feedstock contains a C₄ olefin.
4. The process according to any one of the preceding claim wherein the feedstock contains an olefin of general formula:



wherein R₁ and R₂ are alkyl groups and R₃ may be an alkyl group or hydrogen.

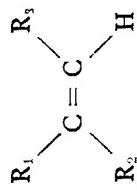
5. The process according to any one of the preceding claims wherein a quantity of hydrogen, sufficient to hydrogenate unsaturated organic radicals produced by the removal of sulphur from the feedstock, is fed to the reaction.

6. The process according to any one of the preceding claims wherein hydrogen is fed to the feedstock contains an olefin in the range C₂ to C₂₀.

WHAT WE CLAIM IS:—

15 1. The process for the desulphurization of an olefin feedstock which comprises contracting the feedstock with supported elemental nickel under conditions such that residual sulphur is adsorbed by the nickel.

20 2. The process according to claim 1 wherein the feedstock contains an olefin in the range C₂ to C₂₀.



- total hydrocarbon fed to the reaction of not more than 1:1.
7. The process according to claim 6 wherein the molar ratio of hydrogen to hydrocarbon is in the range 0.001:1 to 0.1:1.
8. The process according to any one of the preceding claims wherein the supported nickel is pre-sulphided before use.
9. The process according to any one of the preceding claims wherein the nickel is supported on a refractory oxide of an element of Group II to V of the Periodic Table.
10. The process according to any one of claims 1 to 8 wherein the nickel is supported on Kieselguhr.
11. The process according to any one of claims 1 to 8 wherein the nickel is supported on pumice.
12. The process according to any one of claims 1 to 8 wherein the nickel is supported on sepiolite.
13. The process according to claim 12 wherein the nickel on sepiolite contains from 1 to 50% by weight of nickel.
14. The process according to claim 13 wherein the nickel on sepiolite contains from 5 to 25% by weight of nickel.
15. The process according to any of the preceding claims wherein the reaction temperature is in the range 0 to 350°C.
16. The process according to claim 15 wherein the temperature is 20°C to 250°C.
17. The process according to any one of the preceding claims wherein the reaction pressure is in the range 0 to 200 psig.
18. The process according to claim 17 wherein the reaction pressure is in the range 50 to 1000 psig.
19. The process according to any one of the preceding claims wherein the space velocity of the feedstock over the supported nickel is in the range 0.01 to 20 LHSV.
20. The process according to claim 19 wherein the space velocity is in the range 0.1 to 2 LHSV.
21. The process according to any one of the preceding claims wherein the reaction temperature is increased as the ratio of sulphur to nickel in the supported nickel increases.
22. The process substantially as hereinbefore described with reference to the Examples.
23. Olefins wherever desulphurized by a process according to any one of the preceding claims.

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